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Citation	電気材料技術雑誌. 12 p.53-p.56
Issue Date	2003-09-25
oaire:version	VoR
URL	<a href="https://hdl.handle.net/11094/76776">https://hdl.handle.net/11094/76776</a>
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## Photoinduced Surface Relief Grating on the Film of Polyurethane Containing Liquid-Crystalline Azo-Substituent

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The formation of the photoinduced surface relief grating (SRG) on the film of polyurethane containing liquid-crystalline azobenzene in the side chain has been studied. The peak of absorbance of the azo-polymer used in this study is around 360 nm, which is shorter than that of other azo-polymer, such as Disperse Red based, which has been mainly studied so far, and fabrication of SRG with short pitch can be performed using UV light source. Thermal stability of the formed SRG was investigated and discussed on the basis of the glass transition temperature.

KEYWORDS : photochromic polymer; azobenzene polymer; surface relief grating; polyurethane;  
liquid crystal;

## 液晶性アゾ色素を側鎖に有するポリウレタン薄膜における 光誘起表面レリーフグレーティングの形成

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液晶性を示すアゾ色素を側鎖に有するポリウレタン薄膜に、UV レーザーの二光束を干渉させ照射することにより、表面レリーフグレーティングを作製した。他に多くの報告例があるディスパースレッドを側鎖に有するアゾ高分子に比べ、吸収のピークが360nm 付近と短波長であり、光源に短波長な UV レーザーを使用できる分、周期の細かいグレーティングが作製可能となる。また、作製された表面レリーフグレーティングの熱的安定性についても評価し、高分子のガラス転移点に基づく議論も行った。

## 1. Introduction

Recently, a holographic recording of a surface relief grating (SRG) on a thin film of an azobenzene-substituted photochromic polymer upon irradiation of two interfering beams from a low-power laser has been discovered<sup>1,2)</sup>. Many studies have been carried out from the viewpoint of fundamental interest<sup>3-6)</sup> and for practical applications<sup>7-10)</sup>. Due to the cyclic *trans-cis-trans* photoisomerization of azobenzene in the side chain, mass transport is induced to form SRG following the distribution of interfered light intensity. However, the detailed formation mechanism of SRG has not been clarified yet. So far, photoinduced SRG have studied mainly using azo-polymer having acrylate main chain. If polymer main chain is different, novel characteristics reflected by their rheological and mechanical properties can be expected. In this study, formation of photoinduced SRG has been carried out using

polyurethane having liquid-crystalline azobenzene in the side chain.

## 2. Experiment

Figure 1 shows the molecular structure of the polyurethane containing azobenzene moiety in the side chain (L21-TDI) used in this study. The peak of absorbance of the L21-TDI is around 360 nm, which is shorter than that of other azo-polymer, such as Disperse Red based, which has been mainly studied so far, and fabrication of SRG with short pitch can be performed using UV light source. L21-TDI has a melting point at 117°C in heating process. The azobenzene moiety in the side chain (L21) shows liquid-crystalline phase. DSC transition of L21 is summarized in Table.1.

The SRG was formed using the interferential light irradiation system shown in Fig.2. The recording light source was UV light (363.8 nm) of an Ar<sup>+</sup> laser (Beamlok2060-4S: Spectra Physics), and the two recording lights were circularly polarized. Based on the following equation, the periodicity  $\Lambda$  of SRG can be controlled by changing the angle  $2\theta$  between the two recording laser beams.

$$\Lambda = \lambda / 2 \sin \theta$$

Here,  $\lambda$  is the wavelength of the writing laser light. The recorded SRG profile was observed using an atomic force microscope (AFM), (JSTM-4200A: JOEL).

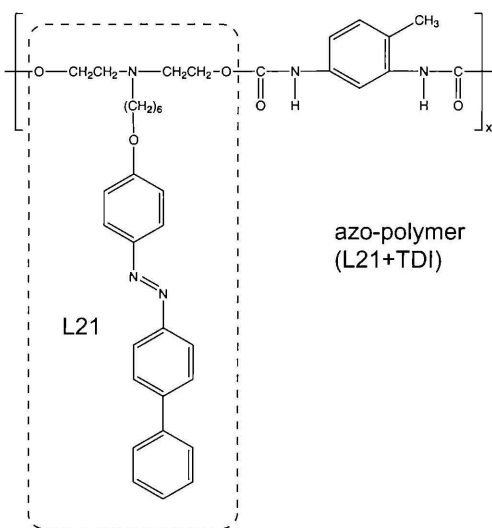


図1 実験に用いたアゾ高分子の分子構造  
Fig.1 Molecular structure of azo-polymer used in this study.

表1 L21のDSC 転移温度  
Table1 List of DSC transitions of L21.

L21	Cooling	129.7 °C	132.6 °C	139.0 °C
	Heating	131.4 °C	133.7 °C	140.2 °C

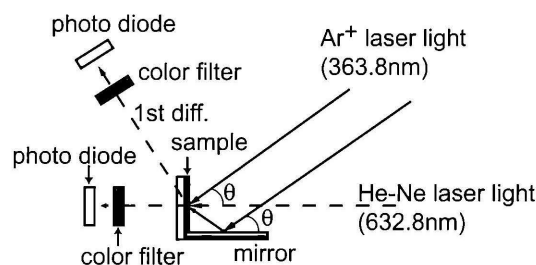


図2 表面レリーフグレーティング作製に用いた干渉光学系  
Fig.2 Experimental geometry for recording the SRG.

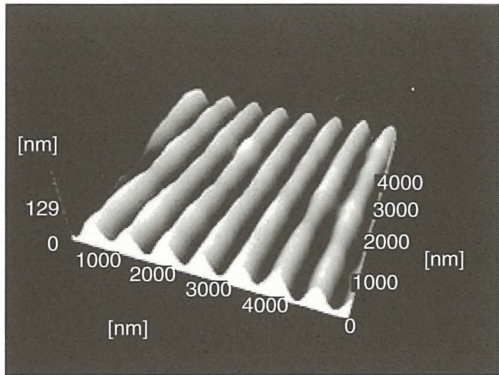


図3 作製された表面レリーフグレーティングの原子間力顕微鏡像

Fig.3 Atomic force microscope profile of the formed SRG.

In order to monitor the formation of SRG *in situ*, the intensity of transmitted and diffracted beams of a He-Ne laser light (632.8 nm) was measured by a photodiode and diffraction efficiency was evaluated as shown in Fig.2. A color filter (O-56: TOSHIBA) which cut off light with wavelength shorter than 560 nm, was placed in front of the detector to prevent the detection of the writing  $\text{Ar}^+$  laser light. The holographic recording was conducted for 90 minutes, and after stopping  $\text{Ar}^+$  laser light irradiation, the diffraction efficiency was also monitored to evaluate the relaxation dynamics under the dark condition.

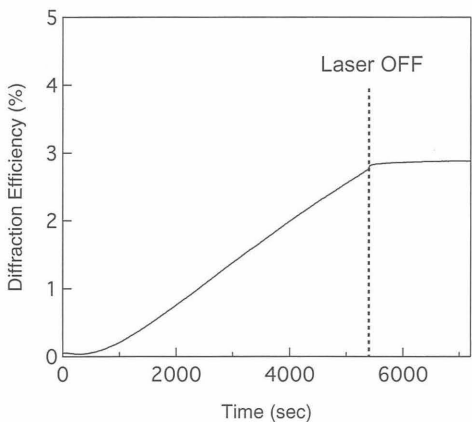


図4 回折効率の書き込み光照射時間依存性  
Fig.4 Writing laser light irradiation time dependence of diffraction efficiency.

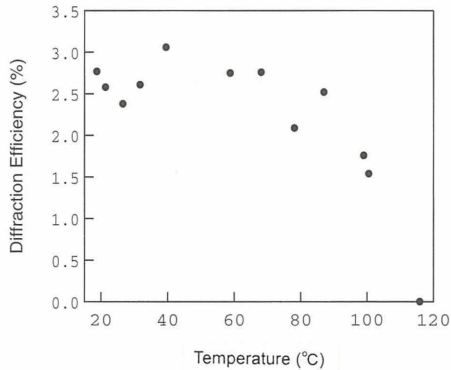


図5 作製された表面レリーフグレーティングの回折効率の温度依存性

Fig.5 Temperature dependence of diffraction efficiency of formed SRG.

### 3. Results and Discussion

Figure 3 shows the AFM profile of the formed SRG on the azo-polymer film. The half angle between two recording laser lights  $\theta$  was  $15^\circ$ . From this figure, it was confirmed that the SRG of about 100 nm in height and 700 nm in periodicity was recorded.

Figure 4 shows the diffraction efficiency of the formed SRG as a function of recording time. Just after the start of recording, the grating structure was formed, and the diffraction efficiency gradually increased by sequential light illumination. This shows that photoinduced fabrication of SRG was performed successfully.

Figure 5 shows the diffraction efficiency of the formed SRG at various elevated temperatures. Diffraction efficiency was stable below about  $80^\circ\text{C}$ , however, at higher temperatures, the diffraction efficiency gradually decreased, and no diffraction was observed more than  $115^\circ\text{C}$ . The melting point of L21-TDI is  $117^\circ\text{C}$ , so that the disappearance of diffraction can be considered as caused by the thermal deformation of formed SRG due to the glass transition of the polymer. This glass transition is lower than that of polyacrylate-based azo-polymer, which has been mainly studied so far ( $\sim 130^\circ\text{C}$ ).

#### 4. Conclusions

The formation of the photoinduced surface relief grating (SRG) on the film of polyurethane containing liquid-crystalline azobenzene in the side chain has been studied. The peak of absorbance of the used azo-polymer is around 360 nm, which is shorter than that of other azo-polymer, such as Disperse Red based, which has been mainly studied so far, and fabrication of SRG with short pitch can be performed using UV light source. Thermal deformation process of the formed SRG was investigated and discussed on the basis of the glass transition temperature.

#### Acknowledgement

This work is in part supported by a Grant-in-Aid for Scientific Research from the Japan Ministry of Education, Culture, Sports, Science and Technology.

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(July 7, 2003 Accepted)